

will on the whole be more favorable for these studies in the region of the lower harmonics and it is hoped shortly to carry out such measurements.

The above was part of a program of work carried out during the tenure of a Leverhulme Research Fellowship, for which I am grateful to the Leverhulme Trustees. I should also like to thank Professor L. Pauling for many kindnesses, and Professor R. M. Badger for allowing me the facilities of his laboratory and for many helpful discussions.

Summary

The absorption bands in the region 8000–11,000 Å. of a series of simple hydroxylic compounds have been measured. The nature of the bands in some cases and the effect of temperature upon them reveals the existence of molecular association in the liquid state. In some cases, such as that of ethanolamine, unusual effects are noticed which cannot be satisfactorily explained.

PASADENA, CALIFORNIA

RECEIVED MARCH 22, 1939

[CONTRIBUTION FROM THE STANDARD OIL COMPANY (INDIANA)]

The Thermal Decomposition of Petroleum Hydrocarbons into Free Radicals¹

BY B. L. EVERING

The free radical chain mechanism proposed by Rice² has been successful in explaining the products obtained in the thermal decomposition of hydrocarbons despite the fact that little is known regarding the concentration of these chain carriers during the reaction. Rice and co-workers² have observed that the Paneth effect of mirror removal by free radicals from hydrocarbons is readily exhibited at 1–2 mm. but not at 20–40 mm. pressure. Patat³ has measured the free radical concentration at higher pressures by the para hydrogen method. He arrived at extremely low values for the free radical concentration.

In the present work the free radical concentrations from petroleum hydrocarbon cuts were investigated in the pressure range where the Paneth effect of mirror removal is exhibited. The radical concentration was followed by combination with a surface of lead freshly formed by condensation of the vapor, and analysis of the product for lead. A rapid decrease of free radical concentration with pressure was found but the complexity of the petroleum hydrocarbon used as a source of free radicals did not permit any exact study of the mechanism. It is hoped that this may stimulate some similar work on the pure hydrocarbons in order to learn more concerning the kinetics of free radical formation and recombination.

Experimental

Materials.—Most of the experiments were carried out using close cuts of petroleum hydrocarbons as a source of

free radicals, while a few were made using butane. The petroleum "octane" had a boiling range 121–130.5°, d^{20}_4 0.7519 and n^{20}_D 1.4173. It had approximately the following composition: paraffins 50%, naphthenes 35%, and aromatics 15%. The petroleum "hexane" used contained 48% C₅ hydrocarbons, 48% C₆ hydrocarbons, the remainder being light and heavy ends. It had the following physical properties: d^{20}_4 0.6653, n^{20}_D 1.3742. The "pentane" used in one experiment was obtained by fractionating petroleum "hexane" in an eight theoretical plate column and taking the cut boiling in the range 34–43°. All of the above cuts were from Mid-Continent crude. The butane and propane were commercial products. They showed no unsaturation and were used without further purification.

The lead used throughout was Baker analyzed, antimony-free. It is important that the lead be antimony-free since free radicals readily react with this metal. This would give low results as the free radical concentration was determined on the basis of the lead alkyls in the product.

Apparatus.—The apparatus shown in Fig. 1 was essentially the same as described by Rice, Johnston, and Evering⁴ with the substitution of lead for mercury, and with certain added refinements to enable quantitative measurements to be made. The hydrocarbon used as a source of free radicals was contained in flask A. The vapor pressure of the hydrocarbon, which was controlled by regulating the temperature of the bath surrounding flask A, was determined by the absolute manometer B. The rate of flow of the hydrocarbon vapor was controlled by the needle valve D which consists of a slender, tapered needle fitted into a concentric tube and both carefully ground. The glass needle was sealed to a glass bulb which floated on a pool of mercury maintained at manometric height so that it could be raised or lowered by adjustment of the attached leveling bulb. In this manner the rate of flow was controlled and kept constant once it had been roughly adjusted by stopcock C.

The rate of flow was measured by the flowmeter E which is of the conventional type. Dibutyl phthalate

(1) Presented before the Division of Petroleum Chemistry at the Milwaukee meeting of the American Chemical Society, Sept. 5, 1938.

(2) F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," Johns Hopkins Press, Baltimore, 1935.

(3) F. Patat, *Z. physik. Chem.*, **32B**, 294 (1936).

(4) Rice, Johnston, and Evering, *THIS JOURNAL*, **54**, 3529 (1932).

was used as a manometric liquid and the instrument was calibrated at reduced pressures for the particular hydrocarbon used. In all cases the flowmeter was used only to keep the rate constant throughout the experiment. The amount of hydrocarbon put through the system, on which the time of contact was calculated, was obtained by volume difference in flask A before and after the experiment.

The reactor L was of transparent quartz and consisted of a side-arm 30 cm. long and 1.0 cm. in diameter on which the heating coil H was wound and in which the hydrocarbons were cracked. This side-arm was sealed onto a 20-cm. length of 4.0-cm. quartz tubing which contained the smaller concentric tube K of 2.8 cm. in diameter onto which a clean lead surface could be continually distilled. The water-cooled tube K was fitted into the reactor by a rubber stopper so that the lower end was just opposite the cracking furnace H. All rubber connections were made vacuum tight with Picein cement. The distance from the mouth of the cracking furnace to the lead surface was 0.9–1.25 mm. depending on the position of tube K. This represents the distance the free radicals must travel before combination with the lead.

The lead was contained in a graphite crucible in the bottom of the large 4.0 cm. tubing directly beneath the tube K. The graphite crucible was 2.5 cm. in diameter and 2.5 cm. deep with a capacity of 20 g. of lead. The free annular space between the crucible and the silica walls was well insulated with Sil-O-Cel. The crucible was heated by inducing a heavy current in it from the induction furnace Z surrounding the reactor at J. The furnace consisted of 30 turns of flattened $\frac{1}{8}$ -inch (3-mm.) copper tubing wound in the form of a helix, insulated between turns and cooled with tap water. The current was supplied from a 3 kw. Ajax high frequency converter which transformed the 220 volt 60 cycle current to approximately 4400 volts and 40,000–50,000 cycles. With this arrangement the lead was readily distilled onto the bottom of tube K at the reduced pressures used in these experiments.

The cracking furnace H varied in length from 10 to 15 cm. and was heated electrically with no. 20 chromel resistance wire. In several runs the diameter of the furnace was varied to test the effect of surface to volume ratio on the recombination of free radicals. This will be considered more in detail under the experimental data. The temperature of the furnace was measured by a platinum-platinum 10% rhodium thermocouple placed in the thermocouple well F directly in the gas stream.

The pressure was read at two points G and X. The pressures reported in Table I are for the reactor and were measured at the point X. The linear velocity of the molecules through the furnace H was calculated for a point at its center, due allowance being made for the pressure drop between G and X. In the first runs at low pressures a small McLeod gage was used. This gage could be read accurately to 10^{-3} mm. at pressures below 1 mm.; however, at higher pressures it could not be used due to the low vapor pressure of petroleum "octane" at room temperature which when compressed would tend to condense. At the higher pressures a direct reading manometer was used, made according to the specifications of Pearson.⁵

(5) T. G. Pearson, *Z. physik. Chem.*, **156A**, 86 (1931).

This manometer had an accuracy of 0.01 mm. at all pressures.

In the early experiments no difficulty was experienced in quickly bringing the whole system to equilibrium, the short time being negligible compared to the long duration of the experiment. In experiments made above 2.0 mm. pressure the runs were of much shorter duration and an appreciable amount of time was required in establishing equilibrium conditions. In these later experiments the condensing system was built in duplicate. The apparatus was operated until satisfactory equilibrium conditions were established and the products were then collected in a clean liquid air trap by manipulation of the mercury level cut-offs M and M'. At the completion of an experiment the liquid air was removed from the trap containing the desired product and placed around the removable trap R. Stopcock O was closed and stopcocks P and Q were opened. In this manner the product was condensed in trap R which could then be removed for analysis.

The apparatus was evacuated to low pressures with a three stage mercury vapor pump backed up with a Cenco-Hyvac pump. In later experiments which were made at high per cent. cracking and at higher pressure the mercury vapor pump was discarded and replaced by a Cenco Megavac pump.

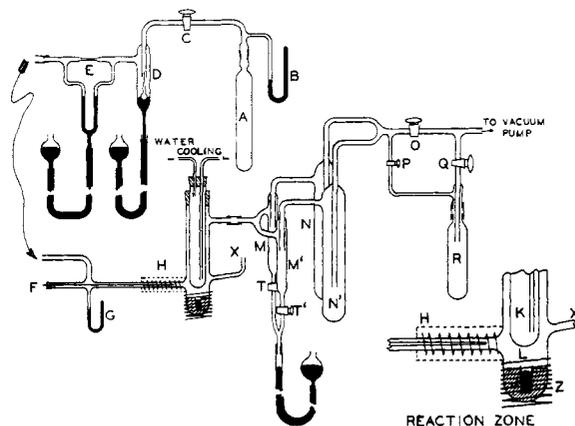


Fig. 1.

In several experiments (13–19) the reactor described in Fig. 1 was replaced with a 2.5-cm. quartz tube 76.0 cm. long. This was wrapped with a heating coil 15 cm. in length and immediately downstream (2.0 cm.) the tube was water jacketed. The lead was placed in a small well in the front section of the furnace which served the dual purpose of volatilizing the lead and cracking the hydrocarbon to free radicals. The lead condensed in the water-cooled section immediately downstream from the cracking furnace where the combination with free radicals occurred in the same manner as on the water cooled tube K in Fig. 1. The modified apparatus is referred to as apparatus B.

Method of Determining the Free Radical Concentration.—The free radical concentrations were determined by analysis of the amount of lead transported by the free radicals from the reactor to trap R in the form of lead tetramethyl. The product obtained from trap R, after vacuum distillation from traps N or N' to remove any colloidal metallic lead, was immediately distilled through a

TABLE I
 DECREASE OF FREE RADICAL CONCENTRATION WITH PRESSURE

Run	Source of free radicals	Apparatus	Press., mm.	Moles	Temp., C.	% cracking	Time of contact, sec.	Linear velocity, cu./sec.	Pb-(CH ₃) ₄ , g.	Moles CH ₃ /Mole paraffin	Moles CH ₃ /Mole paraffin dec.
1	Petroleum "octane"	A	0.25	0.297	1066	37.8	0.0016	6240	0.192	0.0194	0.0512
2	Petroleum "octane"	A	.40	.264	1000	42.5	.0053	2255	.103	.0118	.0278
3	Petroleum "octane"	A	.40	.191	1060	10.3	.0030	3330	.415	.0652	.6320
4	Petroleum "octane"	A	.50	.106	999	9.4	.0017	5740	.219	.0622	.6620
5	Petroleum "octane"	A	.90	.387	1046	28.3	.0031	3160	.271	.0184	.0650
6	Petroleum "octane"	A	1.20	.244	1000	48.0	.0096	1040	.062	.0082	.0172
7	Petroleum "octane"	A	1.80	.297	991	3.3	.0010	10480	.174	.0176	.5320
8	Petroleum "octane"	A	2.10	.362	1037	14.5	.0009	11500	.211	.0174	.1200
9	Petroleum "octane"	A	2.90	.264	982	26.2	.0026	3820	.084	.0096	.0366
10	Petroleum "hexane"	A	3.10	.470	988	37.7	.0088	5760	.083	.0027	.0072
11	Petroleum "hexane"	A	5.50	.089	1107	74.0	.0022	7500	.011	.0019	.0026
12	Petroleum "hexane"	A	5.50	.257	1121	71.0	.0023	7040	.025	.0015	.0021
13	Petroleum "octane"	B	0.52	.528	898	2.0	.0028	5350	.278	.0158	
14	Petroleum "octane"	B	.64	.383	968	15.5	.0034	4360	.301	.0242	
15	Petroleum "octane"	B	1.68	.488	1014	26.0	.0083	1820	.238	.0146	
16	Petroleum "octane"	B	2.67	.507	1038	49.5	.0088	1700	.042	.0024	
17	Butane	B	0.44	.704	982		.0036	4210	.218	.0048	
18	Butane	B	.87	.830	979		.0022	6820	.207	.0039	
19	Butane	B	1.90	.660	1099		.0359	418	.042	.0010	
20	Propane	A	2.00	.507	1201		.0008	20600	.149	.0044	
21	Petroleum "hexane"	A	3.50	.460	1029	23.0	.0029	5170	.086	.0029	.0126
22	Petroleum "hexane"	A	3.50	.480	1023	19.4	.0020	7500	.085	.0027	.0139
23	Pentane dil. with N ₂	A	6.00	.320	1060	69.0	.0026	6350	.019	.0009	.0013
24	Petroleum "hexane"	A	3.00	.540	994	14.8	.0032	15850	.109	.0031	.0209

small column where a cut was made, butanes and lighter hydrocarbons being discarded. The volume was accurately measured and the lead tetramethyl determined by the method of Edgar and Calingaert.⁶ The actual grams of Pb(CH₃)₄ produced in each experiment are shown in column 10 of Table I. The difference between the initial volume passed through the apparatus and the final volume after fractionation was taken as an approximation of the per cent. of cracking. These values are shown in column 7 of Table I.

The calculations of the present work have been based on the assumption that all the free radicals produced from the decomposition of a paraffin hydrocarbon are methyl radicals. This assumption is confirmed by the results of Rice and Evering,⁷ who found that the mercury alkyls obtained from the free radicals produced by the decomposition of butane and contacting with metallic mercury are >95% dimethylmercury. This was further confirmed by fractional distillation and analysis of the products of a number of experiments. As far as could be determined the lead was in the form of lead tetramethyl. There is some question regarding the efficiency with which this method detects all the free radicals formed in the thermal decomposition of a hydrocarbon, though it undoubtedly gives a lower limit. It is not necessary that the method be 100% efficient in detecting the free radicals since the absolute free radical concentration was not being determined but only the change in free radical concentration with pressure in the same apparatus. The only assumption neces-

sary is that the efficiency of the free radical capture by the lead surface does not change with pressure in the same apparatus.

Experimental Results

In Table I the results of twenty-four experiments made under varying conditions are reported. The free radical concentrations expressed in moles (columns 11 and 12) were calculated from the weight of lead tetramethyl, the moles of feed put through the apparatus and the per cent. cracking. The same feed was not used in all the experiments made in apparatus A. Petroleum "hexane" was used instead of petroleum "octane" in the experiments above 3.0 mm. pressure because a more constant feed rate could be obtained under the higher throughput demanded by these conditions. Therefore, in plotting Fig. 2 the moles of CH₃ per mole of paraffin hydrocarbon were used, as the petroleum "octane" contained only 50% of paraffin hydrocarbons from which the major portion of the free radicals should result.⁸

In Fig. 2 the decrease in free radical concentration with pressure, for apparatus A with petroleum "octane" and "hexane," is shown by plotting the logarithm of the values in column 11 for experi-

(6) Edgar and Calingaert, *Ind. Eng. Chem., Anal. Ed.*, **1**, 221 (1929).

(7) Rice and Evering, *THIS JOURNAL*, **56**, 2105 (1934).

(8) Rice, Ruoff and Rodowskas, *ibid.*, **60**, 955 (1938).

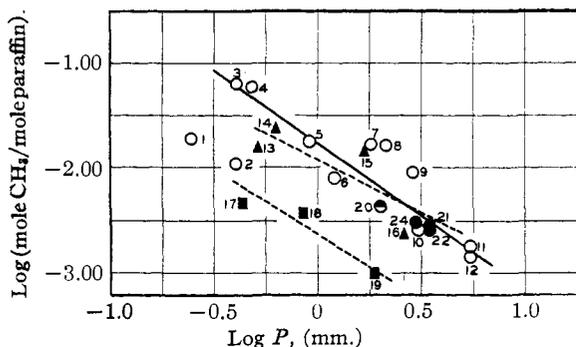


Fig. 2.—Effect of pressure on free radical concentration: petroleum octane, petroleum hexane, apparatus A, —○—; apparatus B, ---▲---; butane, apparatus B, ---■---; propane, ●; furnace dimensions varied, ●.

ments 1 to 12 inclusive against the logarithm of the pressure in mm. There is a scattering of the experimental points due partly to experimental error, to variation in the linear velocity of the molecules through the furnace and the per cent. cracking. It would be desirable, if possible, to obtain a series of curves for the variation of the free radical concentration with pressure under constant conditions of linear velocity and per cent. cracking. Unfortunately not enough experiments were obtained under one set of conditions to permit this. As an alternative the best curve drawn through the scattered points is the solid straight line with the negative slope of 1.37. The slope of the line has no apparent physical significance with respect to the mechanism by which the free radical concentration decreases with pressure.

Table I shows that, although some of the experiments were made under widely varying linear velocities, several experimental points were obtained for various pressures at both high and low linear velocities so that the line drawn as an average of these points is for a mean linear velocity. This is not true in the case of the per cent. cracking. The experiments made above 3.0-mm. pressure were carried out at generally higher percentages of cracking than those below 3.0 mm.-pressure (compare experiments 3 and 4 with 11 and 12) with the result that there is an upward displacement of the straight line in the higher pressure experiments due to the greater depth of cracking. It is possible to separate the effect of the per cent. cracking from the pressure effect by expressing the free radical concentration in column 11 as moles of CH₃ per mole of paraffin hydrocarbon decomposed. This is justified only provided no appreciable error is introduced due

to the decomposition of the naphthenes and aromatic hydrocarbons in the experiments with petroleum "octane."

The logarithms of the free radical concentrations in column 12, Table I for experiments 1 to 12 inclusive are plotted against the pressure in Fig. 3. The experimental points are best represented by a straight line. Extrapolating to zero pressure this line intercepts the y-axis at log -0.16 (a line intercepting the y-axis at log 0 would satisfy the experimental points about equally well). This indicates roughly that each paraffin molecule decomposes initially at extremely low pressures into approximately one free radical. This value cannot be considered too exact because it is not known with what efficiency the free radicals produced in the decomposition are captured on the lead surface and determined as lead tetramethyl.

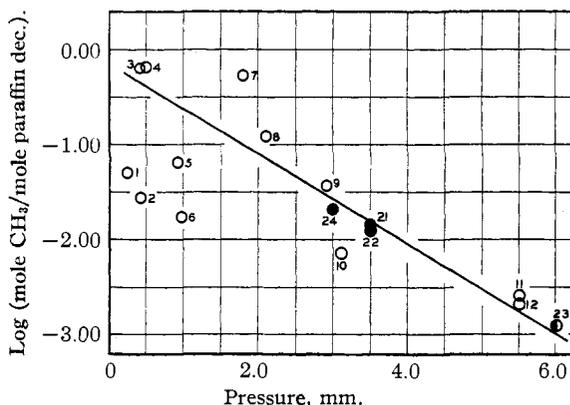


Fig. 3.—Decrease of free radical concentration with pressure for petroleum octane and petroleum hexane: ○, normal operation; ●, furnace dimensions varied; ●, diluted with N₂.

If apparatus A is not 100% effective in capturing the free radicals, the entire line should be displaced upward, giving a higher absolute value for the initial decomposition. However, this uncertainty does not extend to the rate at which the free radical concentration decreases with pressure because only relative values are involved. From Fig. 3 it is seen that in increasing the pressure 15-fold from 0.4 mm. to 6.0 mm. the free radical concentration is decreased 460 fold.

Experiments 13 to 19 inclusive were made in apparatus B. The per cent. cracking was not determined in the butane experiments so that the free radical concentration could not be expressed in terms of moles of paraffin hydrocarbon decomposed. In Fig. 2 the logarithm of the values of column 11 for petroleum "octane" and butane in

apparatus B are plotted against the logarithm of the pressure. The upper dotted line in Fig. 2 represents the best line for the four scattered experimental points on petroleum "octane" in apparatus B. Likewise the best straight line is drawn for the three experimental points on butane. The slope for the disappearance of the free radicals produced from butane in apparatus B is identical with that for petroleum "octane" and "hexane" in apparatus A; while that for petroleum "octane" in apparatus B shows a slight variation. It is probable that this slight variation in slope has no real significance and is due only to experimental error. From the close similarity of the slopes of the lines for petroleum "octane," petroleum "hexane," and butane in apparatus A and B it may be deduced that the free radical concentration is decreasing according to the same mechanism in each case.

The curve for butane falls far below the curve for petroleum "octane" and "hexane." This is to be expected as no correction could be made for the per cent. cracking. Since the cracking temperatures were uniformly the same as those for petroleum "octane," the curve for butane represents a much lower per cent. decomposition than the curve for petroleum "octane" and probably does not mean that butane decomposes into fewer free radicals than the longer paraffin molecules. Additional evidence for this statement is gathered from experiment 20 in apparatus A. This point in which propane was used as the source of free radicals is shown in Fig. 2, and, although not falling on the curve, fits in with the scattering of points from which the line was drawn. It may be concluded that the free radical concentration is not greatly influenced by the source of free radicals (with the probable exception of methane) as long as the temperature is sufficient to give the same degree of decomposition at the same time of contact in each case.

Paneth and Herzfeld⁹ found that the free radicals from lead alkyls recombine mainly along the walls of the tube and by decreasing the surface to volume ratio the half life of the radicals was increased. In experiments 21 and 22 the diameter of the cracking furnace was increased to 1.5 cm., which corresponds to a 41% decrease in the surface to volume ratio from 5.8:1 to 3.4:1. No effect was found as evidenced by the position of these points with respect to the curve as shown

in Fig. 2. A comparison of the results in the larger tube (2.5 cm.) of apparatus B with those of apparatus A (1.0 cm.) is not justified because the relative efficiencies with which the two apparatus captured the free radicals are not known. It might be expected that dilution with nitrogen (or any inert material) would give an increased yield of free radicals under the same conditions per mole of paraffin hydrocarbon decomposed. No increase in free radical concentration was found in experiment 23 when the pentane was diluted with 36.8 mole % nitrogen. Plotting this point in Fig. 3, it falls practically on the straight line expressing the change of free radical concentration with pressure for the experiments in which nitrogen was not present.

Experiment 24 was made to determine the effect of linear velocity on the concentration of free radicals that reached the lead surface. The cracking furnace was elongated from 10 to 78 cm. and the linear velocity of the molecules increased so that approximately the same time of contact was obtained as in the other experiments. The experimental point is shown in Figs. 2 and 3. Increasing the linear velocity approximately threefold had no effect on the free radical concentration within the limits of error of the experimental method.

Discussion

Calculation of the number of wall collisions made by a free radical in passing through the furnace gives a value far too small for this to be a significant factor in explaining the experimental results if an accommodation coefficient of 10^{-4} is assumed¹⁰ together with the time of contact of 10^{-4} sec. This is in agreement with experiments 21 and 22 where no effect was found on decreasing the surface to volume ratio. Recombination of the free radicals must be occurring in the gas phase as each radical makes many hundreds of collisions with other free radicals and the surrounding molecules under these experimental conditions. However, this is not in agreement with experiment 23 in which the pentane was diluted with 36 mole % of nitrogen. The reason for this is unknown.

The rapid decrease of free radical concentration with pressure does explain why the Paneth effect of mirror removal has not been found at 20–40 mm. pressure. On extrapolating Fig. 3 to only 10 mm. pressure, the free radical concentration at

(9) Paneth and Herzfeld, *Z. Elektrochem.*, **8**, 9 (1931).

(10) Paneth, Hofeditz and Wunsch, *J. Chem. Soc.*, 372 (1935).

10% cracking would be about 10^{-6} mole of CH_3 per mole of paraffin hydrocarbon. If it is assumed that the removal of 0.01 mg. of antimony in the form of a mirror can be observed, this would require about 10^{-7} mole of CH_3 . Therefore, the decomposition of approximately one-tenth of a mole of hydrocarbon would be required. It is very probable that the passage of such a substantial amount of hydrocarbon would soon inactivate the mirror due to the products of decomposition and the slight impurities that may be contained in the hydrocarbon before any removal of the mirror could be observed.

It seems plain that at the low pressures used in this work the concentration of free radicals in decomposing petroleum cuts may be very considerable. At the pressures employed in commercial cracking, however, the radical concentration must be very small indeed.

Acknowledgment.—It is a pleasure to acknowledge the assistance of Dr. W. E. Kuentzel in constructing the apparatus and Drs. R. F.

Ruthruff and G. G. Lamb for their help throughout.

Summary

1. The free radical concentrations, as measured by their combination with a metallic lead surface, were determined in the pressure range 0.25 to 6.0 mm. for the following petroleum hydrocarbon cuts: petroleum "octane," petrolatum "hexane," pentane, butane, and propane.

2. A rapid decrease of free radical concentration with pressure was found but the complexity of the petroleum hydrocarbons did not permit any exact study of the mechanism.

3. Dilution of the hydrocarbon stream with nitrogen and decreasing the surface to volume ratio did not noticeably increase the free radical concentration.

4. The molecular weight of the hydrocarbons studied as sources of free radicals had no apparent effect on the free radical concentration when investigated under comparable conditions.

WHITING, INDIANA

RECEIVED MARCH 16, 1939

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Reaction between Maleic Anhydride and Vinyl Hydrindenes

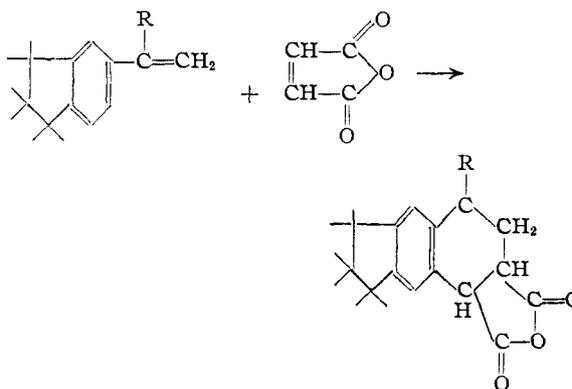
BY RICHARD T. ARNOLD

The conception of stabilized double bonds in condensed ring systems containing one benzene ring was initiated by Mills.¹ In the case of naphthalene and phenanthrene it has been accepted that such bond fixation does occur. For some polynuclear systems, *i. e.*, hydrindene, the problem is completely unsolved although considerable evidence exists on both sides of the question.

It has been shown recently²⁻⁴ that vinyl derivatives of both naphthalene and phenanthrene will add maleic anhydride according to the Diels-Alder reaction. This is extremely interesting in view of the fact that simple benzene derivatives which do not contain a fixed double bond undergo an entirely different type of reaction.⁵ In the single case of *as*-diphenylethylene the normal product is obtained.

With this information as a background, the

corresponding hydrindene problem was studied. If a fixation of the double bonds actually exists in the benzene ring of hydrindene, and if the above reaction with maleic anhydride is characteristic of such fixation, one could expect the formation of the following compound to take place.



On the other hand, if the benzene nucleus in hydrindene is similar to that in styrene a polymer would be formed.

- (1) Mills, *J. Chem. Soc.*, 2510 (1930).
- (2) Bachmann and Kloetzel, *THIS JOURNAL*, **60**, 2204 (1938).
- (3) Bergmann, *ibid.*, **59**, 1443 (1937).
- (4) Cohen and Warren, *J. Chem. Soc.*, 1318 (1937).
- (5) Wagner-Jauregg, *Ber.*, **63**, 3218 (1930).